

# **ELECTROCHEMICAL PROPERTIES IMPROVEMENT OF PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC) USING NANOCOMPOSITE ELECTROLYTE MEMBRANE**

A Mahreni, A. B. Mohamad, A. Amir H. Kadhun and Wan Ramli Wan Daud  
Jabatan Kejuruteraan Kimia dan Proses, Fakulti Kejuruteraan dan Alam Bina  
Universiti Kebangsaan Malaysia  
43600 Bangi, Selangor D.E. Malaysia  
Email: [drab@vlsi.eng.ukm.my](mailto:drab@vlsi.eng.ukm.my)

## **ABSTRACT**

Nafion-Silica oxide ( $\text{SiO}_2$ )-Phosphotungstic acid (PWA) composite membrane have been synthesized using solution phase sol-gel method. The effect of the weight ratio of Nafion: $\text{SiO}_2$ :PWA to the electrochemical properties of composite membrane when applies as electrolyte in the PEMFC was investigated using Fuel Cell Test System (FCTS) at temperature of range of 80 – 90 °C and 40% relative humidity (RH). The weight ratio of the composite membrane samples varied in the range of 100:2.88:1.15, 100:4.33:1.73 and 100:5.76:2.30 and designated as NS10W, NS15W and NS20W, respectively. The aim of the experiment was to insert the inorganic hygroscopic and high conductivity filler like PWA and  $\text{SiO}_2$  in the Nafion matrix to order to improve the water retention, proton conductivity ( $\sigma$ ), hydrogen crossover ( $\beta$ ), and thermal stability in addition to increase PEMFC performance at elevated temperature and low RH condition. The result showed when appropriately embeded in the Nafion cluster, the hydrated PWA and  $\text{SiO}_2$  were endowed in the composite membrane with their high proton conductivity, while retaining the desirable mechanical properties of the polymer film. The water uptake rate and the conductivity of the composite membranes was enhanced with the increase in  $\text{SiO}_2$  and PWA weight content, after which it is reduced when the ratio of Nafion: $\text{SiO}_2$ :PWA became 100:4.33:1.73. However, the conductivity of all the composite membranes were higher compare to the Nafion membrane at cell operation condition of 80 – 90 °C and 40% RH. While hydrogen crossover through the composite is lower than Nafion 112 membrane. This study indicated that Nafion- $\text{SiO}_2$ -PWA composite membrane can be a viable substitute for Nafion for PEMFC which showed good conductivity comparable to Nafion 112 at temperature nearing 100 °C, bearing in mind that Nafion- $\text{SiO}_2$ -PWA composite membranes have better thermal stability.

*Keywords: Nafion; electrochemical processes; hydrogen crossover; PEMFC; composite membrane*

## 1. INTRODUCTION

Many researches have indicated that Nafion membrane (DuPont) as electrolyte of proton exchange membrane fuel cells (PEMFCs) have many weakness that the conductivity will reduced dramatically at high temperatures and low relative humidity causing membrane dehydration and instability fuel cell performances [1, 2, 3, 4]. Due to this reason, the need for modification of the Nafion membrane is crucial in order to enhance membrane conductivity and cell performance stability at elevated temperatures and low relative humidity (RH). Cell operating at high temperature is needed for easy and more efficiency water management, higher reaction rate, improve CO tolerance by anode electro-catalyst, faster heat rejection and better system integration [4, 5, 6]. Therefore, a need exists to develop proton exchange membrane (PEMs) that are functional at high temperatures and low RH operating conditions.

In this study, phosphotungstic acid (PWA) is selected as inorganic filler to enhance conductivity of the Nafion membrane at elevated temperature and low RH because PWA is solid acid with high proton conductivity at room temperature (0.2 S/cm) and has high thermal resistance [7, 8]. The problem is encountered with the particle size and high solubility of PWA in the polar solvent like water and alcohol cause PWA leach out from the membrane when the membrane is applied as electrolyte in the fuel cell [6]. To solve this problem, silica porous particle is used as adsorbent to immobilized PWA and produce the Nafion-SiO<sub>2</sub>-PWA composite membrane. Sol-gel methods have been used to synthesize the Nafion-SiO<sub>2</sub>-PWA composite membrane because it has been shown to improve the composite structure from micro to nanostructure at low temperature condition [9, 10, 11, 12, 13].

Therefore, the main objective of this study to enhance the conductivity of Nafion membrane at moderate temperature (80 – 90 °C) and low RH by incorporation of hygroscopic and high conductivity compound (PWA) into Nafion cluster network using solution phase sol-gel method and study the effect of various Nafion:SiO<sub>2</sub>:PWA ratios in the composite membrane to the electrochemical properties of the composite membrane when its applied as electrolyte in the PEMFC.

## 2. EXPERIMENTAL

### 2.1 Membrane preparation

Appropriately 5% wt Nafion solution was evaporated at room temperature to obtain solid Nafion. Solid Nafion was dissolved in DMF solvent to obtain 5% wt Nafion solution in DMF. PWA was also dissolved in deionised water and then mixed with TEOS at weight ratio of  $\text{PWA}:\text{SiO}_2 = 4:10$ . Subsequently, it was stirred in an ultrasonic bath for 30 min, and added to the Nafion-DMF solution and further stirred in an ultrasonic bath for 6 hours. The mixture was allowed to stand at room condition to release trapped air bubbles for another 24 hours without mixing. This solution was casted in a Petri dish and heated at 80 °C for 2 hours to remove the solvent. In order to enhance the mechanical properties of the composite matrix, heating was continuously applied at 140 °C at different periods of 2, 4, 6 and 10 hours until transparent membrane was obtained. Then, the recast composite membrane was made to detach from the Petri dish by boiling it in the de-ionized water. Finally, the membrane was cleaned by heating at 80 °C in the solution of 3 wt. %  $\text{H}_2\text{O}_2$ , de-ionized water, 0.5 M  $\text{H}_2\text{SO}_4$  and again in de-ionized water until the pH of the washing water becomes almost neutral. These composite membranes are designated as NS10W, NS15W and NS20W, whose specifications in ratio of Nafion/TEOS/PWA are 100:10:1.1538; 100:15:1.7303 and 100:20:2.3072 (wt./wt./wt.), respectively.

### 2.2. Membrane-electrode assembly

Gas diffusion electrodes were fabricated with 20 wt. % Pt on carbon and 0.4 mg Pt cm<sup>-2</sup>. The membrane was sandwiched between the two electrodes and then hot pressed at 130 °C and 70 atm for 90 s to obtain membrane electrode assembly (MEA).

### 2.3. Physico-chemical characterization

Physico-chemical characterizations using Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM) and Fourier Transform Infrared Spectroscopy (FTIR) have previously been reported [18].

An important characteristic of the membrane is the water uptake rate (WUR), which provides information on the water retention ability of the membrane. This is calculated from the difference in weight between the wet and dry samples. The wet weight ( $m_{wet}$ ) was determined after immersion of the samples in water at room temperature for 48 h. As for the dry weight ( $m_{dry}$ ), the samples were heated in the oven at 120 °C for 2 h. The percentage of water uptake rate is thus given as; [7]

$$WUR = \left( \frac{m_{wet} - m_{dry}}{m_{dry}} \right) \times 100\% \quad (1)$$

The thermal stability of the membrane is evaluated by means of thermal gravimetric analysis (TGA) of the type TA 951.

#### ***2.4 Internal resistance (R), conductivity ( $\sigma$ ), hydrogen crossover ( $\beta$ ) determination of the composite membrane and cell performance testing***

The Fuel cell test (FCT) station (FCT-2000 ElectroChem, USA) was used for the cell polarization test and determination of the internal resistance of the membrane. The gas flow of H<sub>2</sub>/O<sub>2</sub> was fixed at the stoichiometric (H<sub>2</sub> + ½ O<sub>2</sub> ↔ H<sub>2</sub>O) mole ratio of 0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was varied between 80 – 90 °C, while the RH was controlled by using the water temperature of the H<sub>2</sub> and O<sub>2</sub> gas humidifiers. During the voltage-current (V-I) measurement, the testing system was stabilized for about 1 h in order to obtain constant value for all the parameters of interest and the resistance of the membranes was measured by optimizing the V-I experiments. The mathematical model for polarization curve was used to correlate the V-I at 40 % RH using least square method. In the V-I model, all resistance parameters were used based on a single fuel cell system, which include the flooding parameter as in Eq 2 [14].

$$E = E_o - b \log(i) - R(i) - \gamma \exp(\omega i) \quad (2)$$

where E, E<sub>o</sub>, b, R,  $\gamma$  and  $\omega$  are the cell voltage, open circuit voltage, Tafel constant, internal resistance, flooding constant and fitting constant, respectively. The internal resistance of the cell is assumed to be same as the conductivity of the composite membrane. Hence, Eq 3 was used to calculate the membrane conductivity [6] as;

$$\sigma = \left( \frac{1}{R} \right) \left( \frac{l}{S} \right) \quad (3)$$

where  $\sigma$  is the conductivity of the composite membrane ( $\text{Scm}^{-1}$ ),  $R$  the resistance (ohm),  $l$  is thickness of the membrane (cm) and  $S$  is contact surface area of the electrode ( $\text{cm}^2$ ).

Hydrogen crossover through the membrane was determined using the open circuit voltage (OCV) data as shown in equation (4) [16]:

$$\beta = 10 \exp [(E_{\text{mix, N}} - E_{\text{mix, m}})/b] \quad (4)$$

where  $\beta$  is the ratio of hydrogen crossover through composite membrane/Nafion,  $E_{\text{mix, N}}$  is OCV of Nafion 112 membrane and  $E_{\text{mix, m}}$  is OCV for the composite membrane.

### 3. RESULTS AND DISCUSSION

#### 3.1 Microstructure of the membrane

The microstructure of the composite membranes has been previously determined [18]. SEM photograph shows the membrane was completely transparent, homogeneous and isotropic in view with a thickness of 70 nm. TEM images have shown the particles size of the composite membrane strongly depend to the ratio between Nafion:SiO<sub>2</sub>:PWA. TEM images showing few particle sizes of about 3-6 nm which should be the PWA nanoparticles. The combination of the TEM and UV data were evident that the particles size is less than the Nafion cluster size suggesting that these particles are embedded in the Nafion cluster. FTIR spectrum of Nafion-SiO<sub>2</sub>-PWA composite membrane is different with the spectrum of Nafion membrane suggesting that the Nafion polymer have been embedded in the structure of Nafion polymer [6, 15, 16, 27].

#### 3.2. Water Uptake Rate (WUR)

The variation of water uptake rate of the composite membranes with that of the commercial Nafion 112 can be seen in Table 1. It is observed that the composite membranes have the tendency to absorb more water than the Nafion 112 sample, which is consistent with other previous studies [10, 20]. The water uptake characteristics of the Nafion-SiO<sub>2</sub>-PWA composite membrane were found to be improved from that of the pure Nafion 112

membrane. The water uptake of the Nafion recast membranes is also increased when the increase in the HPA. This result can be supported from the fact that the hydrophilic characters of the SiO<sub>2</sub> and PWA play a dominant role in the increase water uptake rate of the composite membranes.

Table 1. Water uptake rate of the N112, NS10W, NS15W and NS20W membranes

Membrane	Ratio (w/w) PWA/SiO <sub>2</sub>	Ratio (w/w) SiO <sub>2</sub> /Nafion	Water uptake rate g water/g membrane
N112	0	0	26.52
NS10W	0.4	0.02884	30.25
NS15W	0.4	0.04326	33.43
NS20W	0.4	0.05768	32.72

### 3.3 TGA analysis

The thermal stability of the membrane is usually evaluated by means of TGA. As shown in Fig 1. The TGA of composite membrane indicated that there was a gradual weight loss up to about 290°C. This was due to the evaporation of a little water absorbed, volatile molecule and solvent molecule into the composite membrane during the course of preparation. Upon further heating the composite membrane exhibited a rapid weight loss from 290 °C to 360 °C, corresponding to the decomposition of sulfonic acid groups. It was also show that sulfonic acid groups in the pure Nafion membrane began to decompose at 280°C [7]. From 360-420°C the weight loss was resulted from the decomposition of polar perfluorosulfonic vinyl ether segments and after which, the decomposition of backbone of the Nafion polymer (CF<sub>2</sub>-CF<sub>2</sub>) occurs. The last remainder should be the inorganic phase-SiO<sub>2</sub> and PWA. Similar comparison of the TGA curve of Nafion 112 was also obtained at lower temperature than the start of the decomposition of sulfonic acid group at 280 °C. The TGA results indicated that the composite membrane show higher temperature decomposition compare to the Nafion 112 membrane.

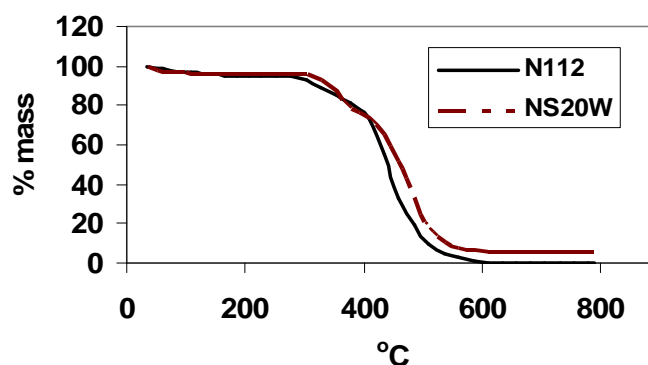


Fig. 1 TGA thermograms of N112 and NS20W composite membrane

### 3.4 Single cell performance

Performance of the single cell membrane electrode assemblies (MEA) using all the membranes (N112, NS10W, NS15W and NS20W), was obtained for the cell voltage versus current density measurement. The results of the test at temperature of 80-90 °C and at 40% RH are presented in Fig 2 (a-b). All the experimental data are presented together with mathematical correlation based on Eq 2 above with volumetric velocity of air at 4.15 L/min, volumetric velocity of H<sub>2</sub> at 1.15 L/min and total pressure of 1.3-1.7 atm. Interestingly, the model shows good fitting correlation with the experimental data for all the membranes under study. The optimized parameters used in fitting the model (Eq 2) with the experiments for all membranes are presented in Tables 2 and 3.

The proton conductivity is decisive property of fuel cell membranes as the efficiency of the fuel cell depends on the proton conductivity. Generally conductivity directly depends on the water uptake rate and ion exchange capacity (IEC) of the polymer membrane. The conductivity of the synthesized composite membranes was compared with that of the commercial Nafion 112 (N112) to ascertain its usefulness. The conductivity of the membrane increases with the increase in temperature. The NS10W, NS15W and NS20W composite membranes exhibited higher proton conductivity than Nafion 112 at low relative humidity (e.g. 40% RH) at two different temperatures. At high temperature and low RH, the membrane experiences cluster shrinkage and increase to the proton hopping resistance and reduced proton conductivity. However, the conductivity of composite membrane of NS10W, NS15W and NS20W the conductivity is higher as compared to the Nafion 112 membrane. This is probably attributed to the retention of trapped water even at high temperature and low relative humidity due to

the capillary condensation effect by the presence of filler PWA particles in the Nafion cluster. The role of the filler when appropriately embedded in the Nafion cluster (hydrophilic Nafion polymer matrix), the hydrated PWA and SiO<sub>2</sub> are expected to endow the composite membrane with their high proton conductivity, while retaining the desirable mechanical properties of the polymer film.

Table 2. Open circuit voltage, Tafel slope, internal resistance, flooding constant and fitting constant for N112, NS10W, NS15W and NS20W membranes, with 70  $\mu\text{m}$  thickness and surface area 50  $\text{cm}^2$  at 90°C and 40% RH.

Membrane	$E_o$ (mV)	$b$ (mV)	$R$ ( $\Omega \text{ cm}^2$ )	$\gamma$ (mV) ( $\varpi=0.01$ )	$i_{maks}$ (mA $\text{cm}^2$ )	$V$ (V)	$P_{maks}$ (W)	Conductivity (S $\text{cm}^{-1}$ ) $10^3$
N112	895.40	43.40	6.01	150.59	31.4	0.32	0.50	1.16
NS10W	890.91	35.58	2.78	135.56	42.7	0.40	0.86	2.51
NS15W	935.87	18.40	2.45	20.00	88.6	0.60	2.66	2.85
NS20W	912.48	16.55	3.01	49.65	69.5	0.52	1.81	2.32

Table 3. Open circuit voltage, Tafel slope, internal resistance, flooding constant and fitting constant for N112, NS10W, NS15W and NS20W membranes, with 70  $\mu\text{m}$  thickness and surface area 50  $\text{cm}^2$  at 80°C and 40% RH.

Membrane	$E_o$ (mV)	$b$ (mV)	$R$ ( $\Omega \text{ cm}^2$ )	$\gamma$ (mV) ( $\varpi=0.01$ )	$i_{maks}$ (mA $\text{cm}^2$ )	$V$ (V)	$P_{maks}$ (W)	Conductivity (S $\text{cm}^{-1}$ ) $10^3$
N112	800.42	44.61	4.56	100.51	33.90	0.32	0.55	1.53
NS10W	803.85	40.99	2.90	107.10	39.80	0.36	0.73	2.41
NS15W	815.86	30.99	2.85	55.10	59.15	0.42	1.27	2.45
NS20W	800.97	37.43	3.31	125.00	42.24	0.36	0.77	2.12



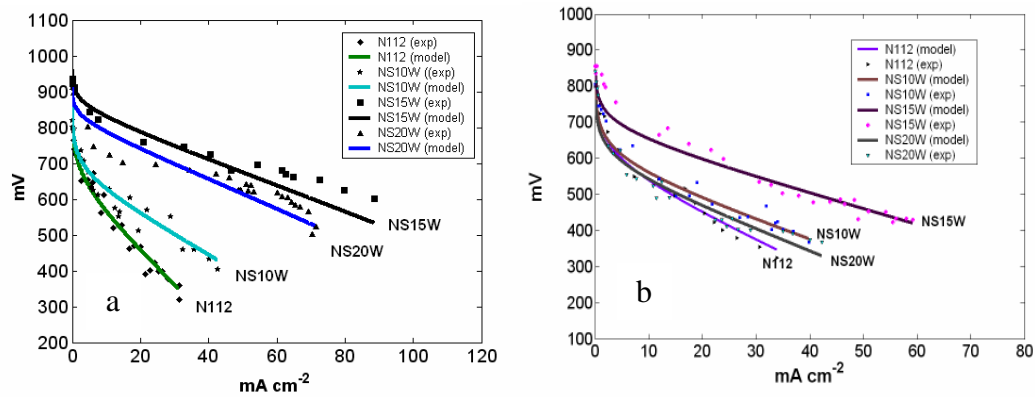


Fig.2. Voltage versus Current density (V-I) characteristics of the PEMFC of Nafion-SiO<sub>2</sub>-PWA composite membranes at (a) 90 °C, 40% RH and (b) 80 °C, 40% RH.

Fig. 2 shows the I-V characteristic of the PEMFC at different operational temperatures. As shows in table 2 and table 3 the open circuit potential of approximately >800 mV is a conventional potential for hydrogen/air cell and indicates there is negligible gas permeability through the membrane [21]. Table 4 list the relative amount of H<sub>2</sub> cross over through the composite membranes and the Nafion 112, calculated by Eq. 4. It can be seen that the amount of H<sub>2</sub> crossover is smaller at temperature 80-90°C and at 40% RH when compared with that of Nafion 112 membrane. The result could to consider that the presence of higher amount of water in the Nafion membrane could fill up the pore of the membrane and suppressed the crossover of gas. The lower amount of H<sub>2</sub> crossover through the composite membrane at (80-90)°C and 40% RH may be owing to the higher water uptake of the membrane as shown in Table 4.

Table 4. Hydrogen crossover through composite and Nafion membrane

Membrane	Ratio of H <sub>2</sub> crossover through Nafion 112/Composite membrane ( $\beta$ )		
	60 °C, 40% RH	80 °C, 40% RH	90 °C, 40% RH
N112	1	1	1
NS10w	0.777	0.823	0.747
NS15W	0.770	0.581	0.006
NS20W	0.906	0.687	0.092

#### 4. CONCLUSION

The incorporation of the inorganic filler PWA ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) into Nafion clusters has resulted in the increased of proton conductivity at moderate temperature and low RH, providing good thermal stability, reduced hydrogen crossover and increase water uptake rate of the composite membrane. TEM measurement indicated that morphology of the membranes is typical of homogeneous material with flexible and very smooth surfaces being obtained. The different particle sizes between TEM and UV analysis showed that the PWA nanoparticles were covered by silica. The water uptake rate increases with increasing the amount of  $\text{SiO}_2$  and PWA and the water uptake rate reaches to maximum when the ratio of Nafion: $\text{SiO}_2$ -PWA reaches 100:4.33:1.728 (wt:wt). The single cell performance test and internal resistance measurement showed that the Nafion- $\text{SiO}_2$ -PWA composite membrane gives better performance at moderate temperature of 80 – 90 °C and 40% RH, especially when the ratio of Nafion: $\text{SiO}_2$ -PWA is 100:4.33:1.728 (wt:wt) as in the case of NS15W. Hence, the composite membrane is shown to be very promising as electrolyte in PEMFC operating at elevated temperatures and lower RH.

#### REFERENCE

1. Smita B. Brijmohan, Shaw, M.T. Proton exchange membranes based on sulfonated crosslinked polystyrene micro particles dispersed in poly (dimethyl siloxane). *Journal of Polymer* 47 (2006): 2856-2854.
2. Hongwei Jang, Baoku Zhu, Youyi Xu. Composite membranes of sulfonated poly(phthalazinone ether ketone) doped with 12-phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) for proton exchange membranes. *Journal of solid state ionics* 177 (2006): 1123-1128.
3. Vito Di Noto & Michele Vittadello. Two new siloxanic proton-conducting membranes Part I. Synthesis and structural characterization. *Journal of electrochimica acta* 50 (2005): 3998-2006.
4. Sacca., A.C, Pedicini, R., Portale, G., Ilario L.D., Longo, A., Mortorana, A. & Passalacqua E. Structural and electrochemical investigation on re-cast Nafion membranes for polymer electrolyte fuel cells (PEFCs) application 1. *Journal of Membrane science* 278 (2005): 105-113.
5. Klein L.C, Daiko, Y., Aparicio, M., Damay. F., Methods for modifying proton exchange membranes using the sol-gel process. *Journal of polymer* 46 (2005): 4505-4509.

6. Ramani, V., Kunz, H.R., Fenton J.M.. Metal dioxide supported heteropolyacid/Nafion® composite membranes for elevated temperature/low relative humidity PEFC operation. *Journal of Membrane Science* 279 (2006): 506-512.
7. Yunfeng Zhai, Huanming Zhang, Jingwei HU, Baolian Yi. Preparation and characterization of sulfated zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ )/ Nafion composite membranes for PEMFC operation. *Journal of membrane science* 280 (2006): 148-155.
8. Ramani, V, Kunz, H.R., Fenton. J.M. Stabilized heteropolyacid/Nafion composite membranes for elevated temperature/low relative humidity PEFC operation. *Journal of electrochimica acta* 50 (2005): 1181-1187.
9. Kukovecz, A., Balogi, Zs., Konya, Z., Toba, M., Lentz, P., Niwa, S.-I., Mizukami, F., Molnar, A., Nagy, J.B., Kiricsi. I. Synthesis, characterization and catalytic application of sol-gel derived silica-phosphotungstic acid composites. *Journal of applied catalysis A: General* 228 (2002): 83-94.
10. Adjemian K.T, Srinivasan, S., Benziger, J., Bocarsly. A.B. Investigation on PEMFC operation above 100°C employing perfluorosulfonic acid silicon oxide composite membranes. *Journal of power sources* 109 (2002): 356-364.
11. Zhijie Li, Wenzhong Shen, Limei Fang, Xiaotao Zu. Synthesis and characteristics of silica-modified ZnS nanoparticles by sol-gel hydrothermal method. *Journal of alloys and compounds* 463 (2008): 129-133.
12. W. Jang, Choi, S., Lee, S., Shul, Y and Han, H. Characterizations and stability of polyimidephosphotungstic acid composite electrolyte membranes for fuel cell, *Polymer Degradation and Stability* 92 (2007): 1289-1296.
13. Kamal M.S. Khalil, Salah A. makhlof. High surface thermally stabilized porous iron oxide/silica nanocomposite via a formamide modified sol-gel process. *Journal of applied surface science* 254 (2008): 3767-3773.
14. J.J. Baschuk and X. Li, Modelling of polymer electrolyte membrane fuel cells with variable degree of water flooding, *Journal of Power Sources*, 86 (2000): 181-196.
15. Mahreni, A., Mohamad, A. B., Kadhum, A. A. H., Daud W. R. W. and Iyuke, S.E. Nafion/silicon oxide/phosphotungstic acid nanocomposite membrane with enhanced proton conductivity (2008). Submission in *Journal of Membrane Science*.

16. Lin, C.W, Thanganuthu, R, Chang, P.H.. PWA-doped PEG/SiO<sub>2</sub> proton conducting hybrid membrane fuel cell application. *Journal of Membrane science* 253 (2005): 23-31.
17. J.D. Kim and I. Honma, Synthesis and proton conducting properties of Zirconia bridge hydrocarbon/phosphotungstic acid hybrid materials, *Electrochim Acta*, 49 (2004): 3179-3183.
18. Staiti, P, Arico, A.S, Baglio, V, Lufrano, Passalacqua F. E. & V Antonucci, Hybrid Nafion-Silica membranes doped with heteropolyacids for application in DMFC. *Journal of solid state ionic* 145 (2001): 101-107.
19. Joongpyo Shim, Heung Yong Ha, Seong-Ahn Hong, In Hwan Oh. Characteristic of the Nafion ionomer-impregnated composite membrane for polymer electrolyte fuel cells. *Journal of Power Sources* 109 (2002): 412-417.
20. Z.G. Shao, P. Joghee, I.M. Hsing. Preparation and characterization of Hybrid Nafion-silica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells, *J. Membrane Sci.*, 229 (2003): 43-51.
21. Itaru Honma, Hitoshi Naajima, Shigeki Nomura. High temperature proton conducting hybrid polymer electrolyte membranes. *Journal of Solid State Ionic*, 154-155 (2002): 707-712.